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Interaction enthalpies of solid human serum albumin with water–dioxane mixtures: comparison with water and organic solvent vapor sorption

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Abstract

Enthalpy changes (ΔH_{tot}) on the immersion of dehydrated human serum albumin (HSA) into water–dioxane mixtures have been measured using a Setaram BT-2.15 calorimeter at 298 K. Thermodynamic activity of water was varied from 0 to 1. Calorimetric results are discussed together with the FTIR-spectroscopic data on water and organic solvent vapor adsorption/desorption isotherms on solid HSA. Dioxane sorption exhibits a pronounced hysteresis. Calorimetric and dioxane desorption dependencies consist of two parts. No dioxane sorption was observed in low water activity region ($a_w < 0.5$). At low water activities, the ΔH_{tot} values are close to zero. At water activity about 0.5 the sharp exothermic drop of the interaction enthalpy values was observed. This exothermic drop is accompanied by the sharp increase in the amount of sorbed dioxane and additional water sorption (compared with that for pure water). Dioxane adsorption branch resembles a smooth curve. In this case, solid HSA binds more than 300 mol dioxane/mol HSA at low water activities. By using a water activity-based comparison we distinguished between dioxane-assisted and dioxane-competitive effect on water sorption. The obtained results demonstrate that the hydration "history" of solid protein is an important factor that controls as the state of protein macromolecule as well as the sorption of low-molecular organic molecules.

Keywords: Interaction enthalpy; Solid protein; Water and organic solvent sorption; Hysteresis phenomenon

1. Introduction

Protein–water [1–5] and protein–organic solvent [6–12] interactions are well known to play an important role in the state and functions of proteins. Knowledge of processes occurring on hydration or dehydration of proteins (hysteresis phenomenon) in the presence of organic liquids is also very important in biotechnological applications of proteins (the catalysts in low water organic solvents [13–16] and use of imprinted serum albumin and some other proteins as selective adsorbents [17]). Hence, the analysis of the thermodynamic characteristics of intermolecular interactions that occur on immersing solid proteins in water–organic mixtures appears necessary in explaining various protein activities.

The interaction enthalpies of proteins with organic liquids might be a very informative property of the intermolecular interactions in such systems. Calorimetry is a reliable method to determine quantitatively this thermodynamic property. For example, based on calorimetric measurements we proposed two different mechanisms of interaction of the hydrated human serum albumin (HSA) with organic solvents [4,18–20]. It was found that in low water pyridine, dioxane, propanol-1, and butanol-1, the water sorption is the only process contributing to the heat effects of interaction of solid HSA with water–organic mixtures. The additional exothermic process was observed when some critical water content was reached. This process was considered to include the rupture of the protein–protein contacts in the solid phase induced by protein–organic component and/or protein–water interactions. On the immersion of solid HSA in binary mixtures of water with acetonitrile, dimethyl sulfoxide, methanol or ethanol, these two

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